Chapter 5

APPLICATIONS: DISPERSIONS, COATINGS, AND OTHER LARGE SURFACE AREA STRUCTURES

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5.1 VISION

In the future, coatings will have improved properties due to nanoparticle incorporations and the methodology of incorporation. Coatings will also be ordered or patterned at the micro- and nano-levels. Similarly, dispersions, powders, and macroscopic bodies with unique morphologies and ordered structures will be discovered. These materials will revolutionize industries dealing with paints, corrosion protection, environmental remediation, drug delivery, printing and optical communications.

5.2 CURRENT SCIENTIFIC AND TECHNOLOGICAL ADVANCEMENTS

The area of dispersions and coatings has seen tremendous advances over the past decades. These advances cover the spectrum from scientific achievements resulting from long-term research to commercial successes. Several significant examples are detailed in the following paragraphs.

Nanostructured and Nanocomposite Films

A new field of scientific research has grown out of the new capability of creating monolayers of organic molecules on substrates (e.g., alkanethiols on gold) with well-organized crystalline order in the monolayer of the organic molecules (Dubois and Nuzzo 1992). A combination of self-assembly with new patterning tools such as microprinting and micromolding (see Xia et al. 1999 and references therein) provides new non-lithographic techniques for creating small patterns on planar and non-planar surfaces.

“Frictionless” films have been discovered over the past five years and promise great economic impact.

Nanostructured emitters like diamond (Zhu et al. 1998) and carbon nanotubes (Zhu et al. 1999) have been demonstrated to have far superior current characteristics compared to conventional field-emitting tips and will play an important role in displays.

Advanced scratch-resistant films of the future will have nanocomposite formulations. In addition, polymeric nanocomposites will enable tunable surface and bulk properties such as adhesion and barrier capabilities.

Organic Templates for Nanoscale Inorganic Synthesis

The discovery of the MCM-41 mesoporous silicate in 1989 at Mobil (Wise 1999) has created a new field in nanotechnology. This process uses liquid crystalline phases to synthesize silica with well-controlled pore sizes in the 1.5 to 10 nm range. Ten years after the discovery of this process, the first commercial products are appearing in the marketplace. Applications include catalysis, filtration, and separation. The same concept has been applied to the synthesis of other nanostructured materials, notably compound semiconductor nanocrystals (Brus et al. 1991) and mesoporous oxides (Yang et al. 1998). Optically transparent magnetic materials for storage applications have been designed using organic templates.

Nanocrystalline Powders and Consolidated Structures

Sol-gel and aerogel/hypercritical drying methods have allowed synthesis of inorganic oxides of huge surface areas with enhanced surface chemical adsorption properties. Under applied pressure these ultrafine powders can be consolidated into highly porous pellets with very large pore volumes and somewhat controllable pore size openings. The surface chemical properties of these ultrafine powders and consolidated pellets seem to be dependent on the unusual polyhedral shapes of the individual nanocrystals, and these materials have found applications as new superadsorbents for toxic chemicals and acid gases (Koper et al. 1997).

Three-Dimensional Assemblies of Nanoparticles

Colloidal gold coated with DNA strands has been used to assay the specific complimentary DNA (Mirkin et al. 1996; Mirkin et al. 1997; Alivisatos et al. 1996). Hybridization of the complementary DNA leads to aggregation of the colloid, accompanied by a color change.

Over the past year several groups have shown that self-assembled colloidal lattices (polystyrene or silica) can be used as scaffolds for inorganic replication. Either sol-gel chemistry or chemical vapor deposition (CVD) processes have prepared titania and carbon replicas (inverse structures) (Holland et al. 1998; Wijnhoven and Vos 1998). Likewise, nanocrystal superlattices (NCSL) of gold and cadmium sulfide/selenide have been formed that exhibit unique optical properties (Lin et al. 1999). These represent new forms of supramolecular crystalline matter. This opens great opportunities to manipulate light via management of void space.

Dispersions and Suspensions with Controlled Fluid Dynamic Properties

Recently, stable water-based ferrofluids have been prepared via organic templates. This has led to advances in colored magnetic inks for printers using magneto-hydrodynamic fluid management in such systems.

Dispersions and Suspension of Hydrophobic Materials

Because pharmaceutical compounds are often hydrophobic, suitable delivery vehicles must be sought (Gardner 1999). Nanoparticle formulations will often allow hydrophobic compounds to be assimilated directly by the body.

Also, as a means of extending imaging systems further, antihalation layers in photographic film systems now contain nanoparticulates to offer specific light filtration for imaging effects. In output media applications for digital printer systems, there are now nanoparticle inks that have been commercialized to achieve image permanency and improved color quality.

5.3 GOALS FOR THE NEXT 5-10 YEARS: BARRIERS AND SOLUTIONS

- Develop nanostructured field emitters (e.g., diamond, carbon nanotubes).
- Further develop the combination of colloidal self-assembly to create three-dimensional periodic structures (nanocrystal superlattices) and replication synthesis of high-dielectric materials (e.g., titania, compound semiconductors, metals, chalcogenide glasses) to produce new materials with interesting optical properties (e.g., photonic bandgap materials). These are likely to find applications in areas such as optical communications and laser technology.
- Further develop the synthesis of nanoscale ceramic materials from dispersions, creating ultrafine powders with new morphologies and composite materials with new properties (e.g., adsorptive, catalytic, thermal, structural, electrical, magnetic, and optical).
- Further utilize the synthesis of inorganic nanomaterials in nonaqueous media.
- If further developed, the next-generation mesoporous silicates and other oxides with highly controlled pore sizes (1 to several tens of nanometers) will play an important role as filters, catalysts, and structural frameworks for the generation of new materials.
- Utilize dispersions (microencapsulated inks, E-ink, Gyricon, Xerox, or polymer-dispersed liquid crystals) as components in electronic paper.
- Develop new ways of self-assembling nanoparticle colloids.
- Investigate synthesis of colloidal particles of controlled non-spherical morphology, (rods, dumbbells, pyramids, etc.). A better understanding of the template materials, such as random polymer matrices, nanotubes, and membranes, is necessary.
- Pursue sol-gel chemistry as a route to high quality silica, already entering the marketplace in the form of preforms for optical fiber manufacturing. With further development, other areas where high quality silica is desired are likely to follow (see Section 5.7.1).

5.4 SCIENTIFIC AND TECHNOLOGICAL INFRASTRUCTURE

- In the area of coatings and dispersions, there is a significant need for better characterization tools, both ex-situ and in-situ (size distributions, morphologies, and interparticle forces). Current tools (light, X-ray, neutron scattering, microscopies, ultrasound spectroscopy, optical spectroscopy, etc.) all have severe limitations and give often model-dependent, average information.

- In this vein, scanning probe microscopies need to be developed to allow multispectral characterization of surfaces.
- Current characterization tools in the sub-optical regime are inherently two-dimensional (scanning electron microscopes, scanning probes, etc.). The discovery of characterization tools of three-dimensional structures at nanometer length scales is highly desirable (e.g., the equivalent of confocal light microscopy in the nanometer regime).
- Access to expensive equipment (transmission electron microscopes, lithography) and large facilities (synchrotrons, spallation sources, reactors, pilot plants for scaleup) should be enhanced, simplified, and facilitated (staffed appropriately).

5.5 R&D INVESTMENT AND IMPLEMENTATION STRATEGIES

- The field of nanotechnology is inherently multidisciplinary and will greatly benefit from strong interactions between universities, industry, and national labs. A general issue that needs to be solved is related to intellectual property: a task force might be able to work out guidelines, thus eliminating the reinvention of the wheel with each new interaction.
- In other fields (e.g., polymers), companies of all sizes exist that do custom synthesis. This capability is lacking in the area of nanoparticle synthesis. It is suggested that SBIRs be encouraged for nanoparticle synthesis, instrument development, and modeling.

5.6 PRIORITIES AND CONCLUSIONS

Nanocrystalline materials represent a bridge between molecules and solid state and exhibit properties that are unique. New coatings and dispersions will take advantage of the huge surface areas and the enhanced chemical reactivities at the surfaces of nanocrystalline materials. These surfaces can be modified with ligands, can be consolidated into porous solids, or can be incorporated into fluids or plastics. Technologies involving inks, magnetics, sorption, catalysis, optical coatings, drug delivery, paints, corrosion protection, and chemical/biological defense are or soon will be affected. However, there is a real need for improved environmentally acceptable synthetic methods for these unusual new materials.

Priorities for the future should emphasize chemical synthesis of nanoparticulate materials, on both the laboratory scale (grams) and pilot scale (kilograms). Academic, government, and industrial laboratories should be working together, and this suggests the need for enhanced funding for individual investigators who are collaborating with industry, and STTR/SBIR funding for academic/government/industry joint efforts. A second priority should be directed at improving methods of characterization, including extending the availability of new instrumentation, with appropriate infrastructure.

5.7 EXAMPLES OF CURRENT ACHIEVEMENTS AND PARADIGM SHIFTS

5.7.1 Optical Fiber Preforms Through Sol-Gel

Contact person: P. Wiltzius, Lucent Technologies

Optical fiber is made from preform cylinders, which are initially several inches in diameter. These glass cylinders are heated and drawn down into fiber with a diameter of typically 0.13 mm. The starting point of an optical fiber preform is commonly a synthetic quartz tube. The cost of these materials is substantial, and alternative manufacturing processes leading to high-quality glass are of great importance to the optical fiber industry.

Sol-gel processing of nanoparticles has emerged as a very promising route to low cost preforms. Typical processing steps include mixing of nanosized colloidal silica and additives, gelation, and casting into molds. A crucial step is the drying of the wet gel body without cracking. After purification (Figure 5.1), the body is consolidated to clear glass.

In addition to a dramatic cost reduction in fiber manufacture, there is also the promise of making novel glass compositions and fiber designs.

Figure 5.1. Photo of sol-gel preforms. The dried, unconsolidated tubes are being loaded into a silica "boat" to be heated in various gases to remove organic compounds, water, and refractory impurities (courtesy Bell Labs/Lucent Technologies).

5.7.2 Nanocomposites: Low-Cost, High-Strength Materials for Automotive Parts

Contact person: J. Garces, Dow Chemical Co.

Requirements for increased fuel economy in motor vehicles demand the use of new, lightweight materials, typically plastics that can replace metal. The best of these plastics are expensive and have not been adopted widely by U.S. vehicle manufacturers. Nanocomposites, a new class of materials under study internationally, consist of traditional polymers reinforced by nanometer-scale particles dispersed throughout (Figure

5.2). These reinforced polymers may present an economical solution to these problems. In theory, these new materials can be easily extruded or molded to near-final shape, yet provide stiffness and strength approaching that of metals—but at reduced weight. Corrosion resistance, noise dampening, parts consolidation, and recyclability all would be improved. However, producing nanocomposites requires development of methods for dispersing the particles throughout the plastic, as well as means to efficiently manufacture parts from such composites.

Dow Chemical Company and Magna International of America (in Troy, MI) have a joint Advanced Technology Program (ATP) project sponsored by the National Institute of Science and Technology (NIST) to develop practical synthesis and manufacturing technologies to enable the use of new high-performance, low-weight "nanocomposite" materials in automobiles (NIST 1997). Proposed potential applications would save 15 billion liters of gasoline and reduce carbon dioxide emissions by more than 5 billion kilograms over the life of one year's production of vehicles by the American automotive industry.

These materials are also likely to find use in non-automotive applications such as pipes and fittings for the building and construction industry; refrigerator liners; business, medical, and consumer equipment housings; recreational vehicles; and appliances.

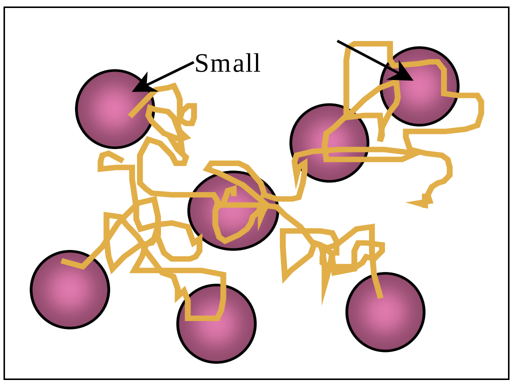

Figure 5.2. Schematic for nanoparticle-reinforced polymeric materials (after Schadler and Siegel 1998).

5.7.3 Biological Weapon Decontamination by Nanoparticles

Contact person: K. Klabunde, Kansas State University

Ultrafine powders can decontaminate mimics of biological weapons. For example, airborne heat-resistant *Bacillus Globigii* spores (a mimic for Anthrax) are killed at room temperature by airborne nanoparticles formulated from magnesium oxide and other reactive components. Figure 5.3 shows how the colony forming units (CFU) of *Bacillus Globigii* are detoxified over a 5-20 minute period. Similarly, *Bacillus Cereus* spores or *E. coli* bacteria can be disinfected. Several nanoparticle formulations have been shown to be effective, whereas commercial powders of the same materials are not.

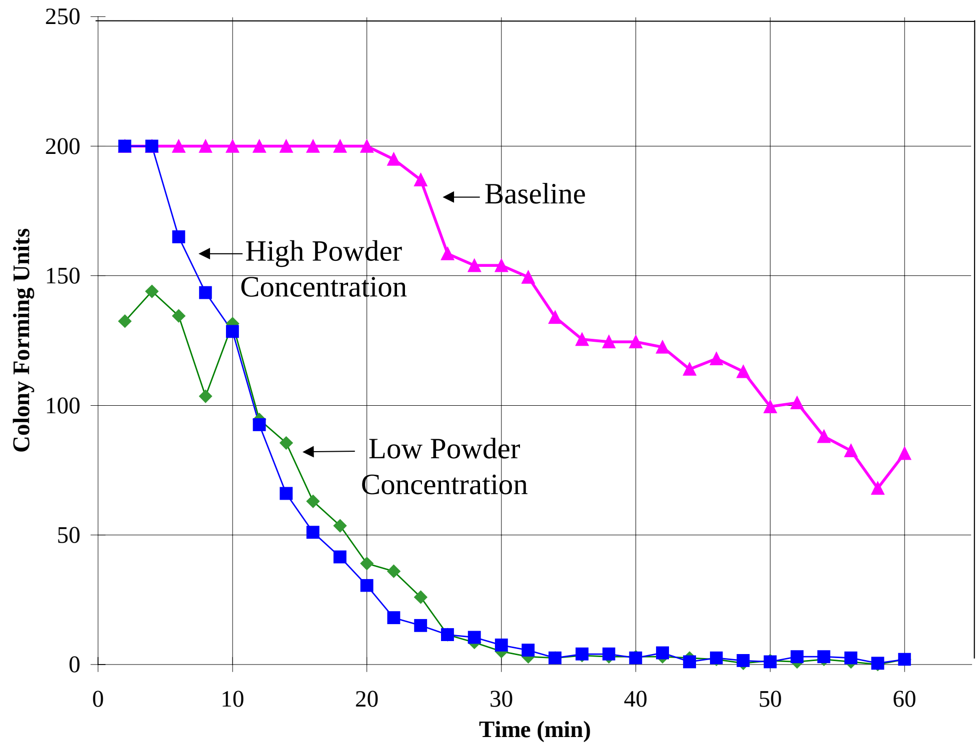

Figure 5.3. Decay curve for *Bacillus Globigii* baseline and *Bacillus Globigii* with chlorinated nanoparticle powder. It shows a baseline and two curves (each reproduced by two Brunswick air samplers), one for low nanoparticle concentration (10 mg/m^3) and one for a higher nanoparticle concentration (20 mg/m^3) in the air.

5.7.4 Nanoparticles for Use in Imaging Systems

Contact person: J. Mendel, Eastman Kodak Co.

Ability to generate thinner imaging layers is a consequence of using nanoparticulate preparations in image-recording layers such as graphic film systems; the high surface area of nanoparticulate filter dyes allows for higher feature performance and results in the ability to reduce the concentration of the dye component. In addition, the use of nanoparticulates in graphic film applications produces filter dye layers that have less light scatter by virtue of the finer particle size. This reduced light scatter leads to sharper absorption spectra, allowing for controlled handling of the film under specified light conditions.

Another advantage from nanoparticulate preparations of these filter dyes comes from the use of the polymeric media in the size reduction process. The polymeric media avoids creating attrition products, as are common with ceramic or metal media. The latter materials often produce pH changes, which adversely cause the dye to wander in the coating. Many attrition products affect dispersion stability and change the size reduction performance by influencing the final particle distribution of the slurry. Attrition products degrade milling performance and increase manufacturing maintenance costs. The polymeric media used in preparing nanoparticle slurries avoids those deficiencies, which results in a more invariant process for slurry preparation (U.S. Patents #5478705, 5442279, and 5474237).

5.7.5 Applications of Magnetic Fluids Containing Magnetic Nanoparticles

Contact person: T. Cader, Energy International, Inc.

Ferrofluids, first manufactured in their present-day form in the early 1960s, are colloids consisting of magnetic nanoparticles (10 nm in diameter) that are coated with a surfactant to ensure stability and suspended in a carrier such as transformer oil, water, or kerosene. The nanoparticles are individual permanent magnets, and when placed in suspension, the net magnetization of the ferrofluid is zero until a magnetic field is applied (see Figure 5.4). For example, a rotating magnetic field will align the nanoparticles, giving rise to a non-zero ferrofluid magnetization, while at the same time rotating the individual nanoparticles, as well as the ferrofluid itself, through entrainment of the carrier fluid. What distinguishes ferrofluids from other fluids are the body and surface forces and torques that arise in the ferrofluid when magnetic fields are applied to them, which in turn give rise to unusual fluid mechanical phenomena (Rosensweig 1985). Magnetic fluids such as magnetorheological suspensions employ larger particles (>100 nm), and unlike ferrofluids, tend to "freeze up" in intense magnetic fields.

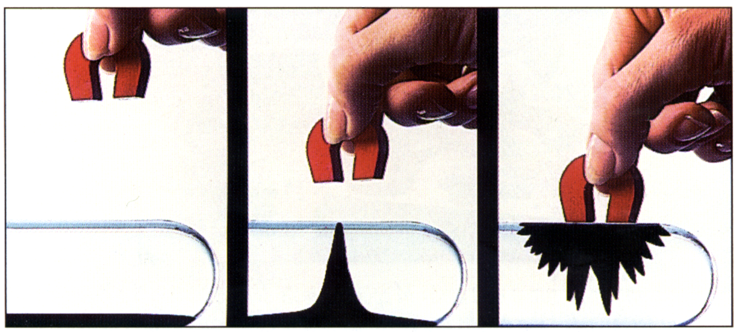

Figure 5.4. Visualization of a ferrofluid immersed in water (courtesy of Ferrofluidics Corp.).

Short-Term

Present-day applications require very small volumes of ferrofluids (~10 ml). This is one of the key reasons for current high prices of these fluids. Current applications, which have an estimated total market size of ~$30-60 million, include the following:

- Contaminant exclusion seals on almost every PC disk drive manufactured, in silicon crystal-growing furnaces for the semiconductor industry, and in the medical field in MRI and CAT scan equipment
- Vacuum seals for high-speed, high-vacuum, motorized spindles
- Use as viscous dampers in the air gaps of stepper motors used in aircraft and various other machines

Medium-Term

Other applications are expected in three to five years. The success of key medium-term applications hinges in large part upon the advancement of the science of the behavior of ferrofluids subjected to time-varying and steady magnetic fields, for both heated and isothermal scenarios. For the time-varying fields, additional knowledge is necessary relating to the theory, including the appropriate boundary conditions for spinning nanoparticles at a wall. For all applications, good knowledge of the thermophysical properties (including dielectric properties) of the ferrofluids is essential. Medium-term applications currently under development include the following:

- Enhanced cooling and electrical insulation of power transformers
- Magnetic separation of ores in mining, and scrap metal separation

Success in any one of these high volume applications will lead to a significant reduction in ferrofluid pricing levels and will open the door to many more applications. For example, the potential market (in terms of revenue) for ferrofluid transformers lies in the range of $0.5-1 billion; in addition, there will be substantial savings to utilities.

Longer-Term

Applications for the longer term (over five years) are very promising. A host of exciting long-term applications are discussed in the literature. NASA's center for microgravity research is investigating how ferrofluids can play an important role in space, where gravity is essentially absent and free convection-dependent processes can be sustained by replacing the gravitational force with a magnetic force. In addition, through magnetic manipulation of the magnetic nanoparticles, ferrofluids offer a unique opportunity to remotely control the pressure, viscosity, electrical conductivity, thermal conductivity, and optical transmissivity of a fluid. Long-term applications also include the following:

- Development of ferrofluid-cooled and insulated power equipment for extended human space missions
- Development of nanoscale bearings that simultaneously levitate and lubricate a rotating shaft inside a bushing
- Magnetically controlled heat conductivity for precision temperature control of small devices such as electronic components

5.7.6 Summary of Current and Potential Applications

Contact person: J. Mendel, Eastman Kodak Co.

Table 5.1 summarizes current and potential future applications of nanostructured materials in the high surface area, coatings, and dispersions areas. More specific product applications are summarized below:

Commercial Applications Within the Next Three Years

- Use of nanoparticle metal oxides for decontamination of military warfare agents, which would be of great benefit to military personnel and useful for combating terrorism
- Use of nano, micro- and mesoporous composites (porous pellets) for air purification and disinfection, for example for airplanes and buildings
- Use of silica nanoparticles for manufacture of optical fibers

Commercial Applications Within the Next 5 Years

- Storage of information on transparent films or disks
- High quality magnetic inks
- Commercial firms offering custom nanoparticle syntheses
- Nanocrystalline superlative arrays used for the manufacture of new lasers
- A wide variety of new medicinal compounds
- Higher strength nanoparticle-polymer composites available to automobile and other industries
- More selective, efficient catalysts and sorbants and gas separation membranes

Table 5.1. Present and Future Applications of Nanostructured Dispersions

Now	3-5 years	Long term
Thermal barriers	Targeted drug delivery areas	Large fuel and energy advances from nanoparticles in fabrication and transportation
Optical (visible and UV) barriers	Gene therapy	Nanotechnology for improved environmental needs
Inkjet materials	Multifunctional nanocoatings	Nanoparticles for prosthesis and artificial limbs
Coated abrasive slurries	Nanocomposites for automobiles, weapon systems	Nanoparticles for integrated nanoscale sensors
Information recording layers	Nanocomposites for lighter, corrosion-resistant materials	Nanocomposites for space exploration uses
	Nanotechnology for taste enhancers, cosmetics, and other personal uses	Synthesis of nanomaterials in liquid nonaqueous media
		Next-generation mesoporous oxides
		Nanoparticles for decontamination

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